taken between the proper limits. The terms divided by $n' + n$ having but a small coefficient in the numerator, and having a denominator which is not small, may be left to take their chance with casual fluctuations; but the terms divided by $n' - n$ rise into importance from the smallness of the denominator, and express an inequality in the integrals of comparatively large amount and long period.

We may therefore confine our attention to the terms

$$\frac{c}{2(n'-n)} \sin\left[(n'-n)t+\alpha\right], \qquad \frac{c}{2(n'-n)} \cos\left[(n'-n)t+\alpha\right],$$

occurring in the indefinite sine integral and cosine integral respectively.

If, therefore, the values of these two integrals, obtained from the two cylinders respectively, be plotted, we shall obtain a periodic fluctuation of a period more or less long as we hit on a period more or less near to that of the inequality which we have supposed to exist. The zero points of the fluctuation in the sine integral will correspond to the maxima and minima in that of the cosine integral, and *vice versâ*. The reciprocal of the period of the fluctuation will give the difference of the reciprocals of p and p', and thus p' will be known from p provided only we know which of the two, p, p', is the greater. This will be shown by comparing the phases of the fluctuations of the two integrals. If $n' > n$, the fluctuation of the cosine integral will be a quarter of a period behind, if $n' < n$ before, that of the sine integral.

If $f(t)$ be subject to known periodic inequalities with approximately known coefficients, the integrals should be cleared of the terms thence arising, if of sufficient moment, by using their analytical expressions, and the residues only plotted.

Of course $f(t)$ is not necessarily a function of the time given by *direct* observation; it might be a function deduced from one so obtained. For example, $f(t)$ might be the coefficient of the principal term in the daily fluctuation of the element when each day's record is separately subjected to harmonic reduction.

May 29, 1879.

IV. Researches on Explosives. No. II. (Fired Gunpowder.). By Captain NOBLE, late R.A., F.R.S., F.R.A.S., F.C.S., and F. A. ABEL, C.B., F.R.S., V.P.C.S. Received May 21, 1879.

(Abstract.)

The authors preface this memoir by two tables : one of these gives the results of some analyses of products of explosion of the three service powders of Waltham Abbey manufacture, pebble, R.L.G. and F.G., which are required to complete the series of results obtained by

firing the charge in different spaces, which were given in their first memoir on this subject, and a statement of the mean percentage composition by volume of the gases and by weight of the solid products furnished by those three powders, together with the highest and lowest proportions in which each product has been obtained with the three descriptions of powder. This table includes the results of examination of the products of explosion of four descriptions of powder differing in many respects from the powders chiefly employed in their researches. The other table gives the complete results of the whole series of analyses made, showing the proportion by weight of each solid and gaseous product, and including the amount of water preexistent in the various specimens operated on.

The following abstract of the table first referred to includes the analytical results of the products furnished by the four special samples of powder, and the highest, lowest, and mean proportions of the several products furnished by the three principal powders used. (See next page.)

A portion of this memoir is devoted to a discussion of a few points raised in reference to the first memoir of the authors, on fired gunpowder, by General Morin and M. Berthelot, who were appointed by the Académie des Sciences as a Commission to report on that memoir. These points were specified and discussed by those savants in a joint report, and in two separate memoirs communicated by M. Berthelot to the Académie.

The principal points to which attention has thus been drawn are as follow :—

1. Potassium hyposulphite has been found as one of the products of combustion of gunpowder by every recent investigator. But the question arises : Is this product either wholly or in part primary ? or is it to be considered as secondary, formed from the primary products during the rapid loss of heat to which they are exposed ? or is it, finally, to be considered only as formed from the sulphide by the absorption of oxygen during the processes of removal from the cylinder and analysis, and therefore to be regarded as an accidental product ?

2. The authors, from their investigation of the products of explosion in gunpowder in close spaces, conclude that "any attempt to express, even in a complicated chemical equation, the nature of the metamorphosis which a gunpowder of average composition may be considered to undergo, would only be calculated to convey an erroneous impression as to the simplicity or definite nature of the chemical results and their uniformity under different conditions, while possessing no important bearing upon an elucidation of the theory of the explosion of gunpowder."

M. Berthelot, in one of his memoirs based upon the authors' results, proposes to represent these results by a system of simultaneous equa-

Nature of powder.		Percentage composition by volume of the gas.							Percentage composition by weight of the solid residue.										
		Carbonic anhydride.	Carbonic oxide.	Nitrogen.	Sulphydric acid.	Marsh-gas.	Hydrogen.	Oxygen.	Potassium carbonate.	Potassium sulphate.	Potassium hypo-sulphite.	Potassium mono-sulphide.	Potassium sulphocyanate.	Potassium nitrate.	Potassium oxide.	Ammonium sesqui-carbonate.	Sulphur.	Charcoal.
Pebble W.A.	Means	48·94	13·70	32·14	2·60	0·31	2·34	...	57·17	12·46	13·89	10·25	0·27	0·23	...	0·10	5·45	0·15
	Highest	51·75	16·09	32·75	4·23	0·68	3·50	...	64·20	15·02	32·18	19·12	0·57	0·48	...	0·17	8·45	1·35
	Lowest	44·78	10·87	31·31	1·70	0·00	1·67	...	50·20	9·13	3·71	2·23	0·06	0·00	...	0·06	0·61	trace.
R.L.G. W.A.	Means	49·47	12·47	32·91	2·65	0·43	2·19	0·06	59·05	14·58	13·20	6·27	0·22	0·26	...	0·07	6·26	0·07
	Highest	52·65	17·04	35·60	4·29	0·84	3·01	0·57	66·51	24·22	25·33	9·92	0·49	0·56	...	0·18	12·03	0·71
	Lowest	46·29	8·98	30·29	1·56	0·00	1·27	0·00	48·68	4·64	3·08	2·02	0·05	0·00	...	0·04	1·25	trace.
F.G. W.A.	Means	50·62	10·46	33·20	2·48	0·19	2·96	0·08	48·31	21·11	24·79	2·41	0·12	0·16	1·29	0·05	1·75	
	Highest	53·34	16·25	34·64	3·76	0·50	4·13	0·28	59·39	24·22	34·61	5·12	0·25	0·26	5·39	0·15	5·72	
	Lowest	44·76	7·71	32·22	2·00	0·00	2·04	0·00	41·88	17·86	5·30	0·00	0·02	0·08	0·00	0·01	0·09	
Spanish Spherical	70 per cent.	53·34	4·62	37·80	2·74	...	1·29	0·21	34·97	47·62	7·60	3·17	0·04	0·93	...	0·04	5·63	
Curtis and Harvey, No. 6	30 per cent.	50·22	7·52	34·46	2·08	2·46	3·26	...	58·51	21·43	3·93	10·02	...	0·29	...	0·09	5·73	
Mining Powder	30 per cent.	32·15	33·75	19·03	7·10	2·73	5·24	...	40·78	0·58	5·84	33·20	2·92	0·09	...	1·76	12·93	2·00

tions expressing the chemical metamorphosis undergone by powder, at least as far as regards its fundamental products.

3. In directing attention to the determination by the authors of the heat disengaged by the explosion of powder (the results of which were put forward by them with some reserve), MM. Morin and Berthelot regard the figure arrived at as too low, partly because of a deficiency in delicacy of the apparatus, and partly because higher figures have been arrived at by M. Tromenec and by MM. Roux and Sarrau.

In discussing M. Berthelot's views respecting the objections which the authors raise against the acceptance of any chemical equation as giving even a general idea of the metamorphosis which a gunpowder of average composition may be considered to undergo when exploded in a confined space, they disclaim having had any intention to convey the impression, which indeed they consider that their expressions were not calculated to convey, that it was impossible to put into *some* form of equation a representation of a variety of reactions which, if assumed to take place simultaneously, among different proportions of the powder-constituents, might give approximate expression to the results obtained in any one particular experiment, and might, thus far, afford some approach to a theoretical representation of the metamorphosis of gunpowder.   What they desired to point out and lay stress upon was the conclusive proof, which is afforded by the very great variations in composition, of the solid portions more particularly, of the products of explosion of samples of gunpowder presenting only small differences of composition (and even of the products furnished at different times by one and the same sample), that the reactions which occur among the powder-constituents are susceptible of very considerable variations, regarding the causes of which it appears only possible to form conjectures, and that, consequently, " no value whatever can be attached to any attempt to give a general chemical expression to the metamorphosis of gunpowder of normal composition."

Starting with the assumption (which the authors cannot admit to be a correct interpretation of their view) that they regard the variations which occur in the principal products of explosion as "opposed to all general chemical representation of the metamorphosis produced by explosion," M. Berthelot proceeds to argue that the formation of those products, viz., of carbon dioxide, carbon oxide, potassium sulphate, sulphide and carbonate from a powder of normal composition, is simply and satisfactorily accounted for by assuming the simultaneous occurrence, in variable proportions, of either *three* or *four* out of *five* different theoretical reactions, according as to whether the proportion of sulphate found is so small that it may be neglected, or amounts to 12 or 14 per cent.

After giving further equations which apply to the extreme results

(in regard to the chief products only) assumed to be attainable from
the introduction, on the one hand of excess of saltpetre, on the other
of excess of charcoal, into the composition of powder, M. Berthelot
passes to what he terms the accessory products and, excluding from
these potassium hyposulphite, which he deals with separately, he first
gives *two* equations to account for the production of sulphocyanide;
then *two more* to explain the existence of ammonium sesqui-carbonate
(which he believes to be formed by the action of water vapour on
potassium cyanide); the existence of sulphuretted or free hydrogen is
explained by *two more* equations, and marsh-gas is assumed to result
from " the pyrogenous decomposition of the charcoal in the powder."
Lastly, an equation is given to account for the possible formation of
traces of hyposulphite, which Berthelot however regards entirely as a
product formed during the collection and analytical treatment of the
solid residue, but which the authors nevertheless believe they now
conclusively prove to be formed in very notable quantities before the
solid residue can have undergone alteration from external causes.

It will be seen from the foregoing outline of M. Berthelot's theo-
retical explanation of the chemical changes involved in the metamor-
phosis of gunpowder, that the simplest form of expression which he
can give to the formation of the products of explosion consists in the
incorporation of *nine* or *ten* distinct reactions, occurring simultaneously
but in very variable proportions, which have to be supplemented by
three or *four other* chemical equations, by which the formation, during
the process of cooling of certain products believed to be secondary, is
explained. Now, although such speculations as the above are un-
questionably interesting, and, it may be added, of a nature which
must occur to those who desire to give some kind of definite explana-
tion, for purposes of elementary instruction, of the chemical changes
involved in the explosion of powder, the authors fail to see that, beyond
this, they do more than afford the strongest confirmation of the cor-
rectness of their conclusion, that " no value whatever can be attached
to any attempt to give a general chemical expression to the metamor-
phosis of a gunpowder of normal composition."

With reference to the potassium hyposulphite, which, in the
analyses of the solid products published in the first memoir, ranged
from 3 to 35 per cent. (the monosulphide being generally small in
amount when the proportion of hyposulphite was high), the authors
reply to M. Berthelot's suggestion, that its existence may be only
ascribable to the oxidation of sulphide during the operation of
removal from the explosion-vessel and of analysis, by pointing out the
nature of the precautions taken to avoid oxidation of sulphide in the
collection of the solid residue, and its preservation for analysis, and
by admitting the formation of some hyposulphite during the unavoid-
able exposure to air of the residues while they were being removed

from the cylinder, especially in some instances when the structure of
the residue was favourable to atmospheric action, and when the
development of heat afforded proof of the occurrence of such oxida-
tion.   They point out, on the other hand, that no hyposulphite could
be accidentally formed from sulphide during the analytical operations
as carried out by them, and they proceed to show that the very con-
siderable variations in the amount of hyposulphite, as well as the
large amount of sulphide found in several instances, in distinct
operations conducted with very great uniformity, afford substantial
proof that accidental atmospheric oxidation during the collection and
analysis of the residues, is not sufficient to account for all but the very
small quantities of hyposulphite which M. Berthelot considers could
only have pre-existed in the residue examined by the authors.

They furthermore direct attention to the following facts given
in their first memoir, which appear to have been overlooked by
M. Berthelot.

· 1. Separate examinations (conducted precisely alike) of the upper
and lower portions of some of the residues, showed that considerably
larger proportions of hyposulphite existed in the *upper* portions.   In
one case, quoted by them in their first memoir, the upper portion con-
tained 17·14 per [cent. of hyposulphite, while the lower portion only
contained 4·34 per cent.   At the same time there was only a difference
of 1·27 per cent. in the proportions of monosulphide existing in the
two portions of the residue (6·03 in the upper part and 7·3 in the
lower), while there was a very great difference in the amount of free
sulphur (4·88 in the upper part and 10·09 in the lower).

2. One of the small buttons of the fused solid products, of which
there was generally one found attached to the firing plug in the
cylinder, was examined for sulphide and hyposulphite (it having been
detached without fracture and at once sealed up in a small tube).   It
contained the latter, but none of the former, while the mass of the
residue of this particular experiment contained a somewhat consider-
able proportion of sulphide.

3. The production of high proportions of hyposulphite was but
little affected by any variations in the circumstances attending the
several explosions (*i.e.*, whether the spaces in which the powder was
exploded were great or small), excepting that the amount was high in
all three cases when the powder was exploded in the largest space.
The analytical results given in the earlier memoir show abundantly,
on the other hand, that a great reduction in the size of grain of the
powder used had a great influence upon the production of hypo-
sulphite.

Although the authors consider that the formation of hyposulphite
in the solid residue, before the explosion-vessel is opened, and, indeed,
to such an amount that it must be regarded as an important product

(whether primary or secondary) is conclusively demonstrated by a thorough examination into the results given in their first memoir, they have been anxious to obtain, if possible, some further decisive evidence as to the probable proportions of hyposulphite actually existing in the residues furnished by the explosion of gunpowder in closed vessels. They, therefore, introduced some variations in the methods of collecting and preparing the solid products for analysis, of which the following is an outline.

In two experiments with R.L.G. and pebble powders, the solid products, collected as rapidly as possible, were divided into two equal parts, the one consisting of the upper, the other of the lower, part of the mass. These portions were again equally divided; one-half, composed of large lumps, was as rapidly as possible (being but a few moments exposed to air) sealed up in dry bottles freed from oxygen; the other half of each was ground finely and exposed to the air for forty-eight hours.

In both experiments the lower ground portion heated very decidedly more than the upper part, the tendency to heat being abnormally high in the case of the pebble residue; a thermometer inserted into the ground mass indicated a temperature of 315° C. After half an hour's exposure the deposit cooled very rapidly.

The products obtained in these two experiments were submitted to partial examination, the chief object being to see to what extent the proportions of hyposulphite and sulphide varied in the upper and lower portions of the residue, and the extent to which they were affected by the great difference in the mode of treatment sustained by the different portions of one and the same residue.

The numerical results obtained show that, in both experiments, those portions of the residue which were exposed to the air only for a few seconds, and of which but small surfaces *were* thus exposed (as they were collected in large lumps) contained hyposulphite ranging in amount from 5 to 8·5 per cent. Those portions which were specially treated for the purpose of favouring to the utmost the formation of hyposulphite from sulphide through atmospheric agency, contained, as was to be expected, very large proportions of the former, while the latter had entirely disappeared in three out of the four portions of very finely pulverised residue. In the fourth, however, even after its free exposure to air for forty-eight hours, there still remained nearly 3 per cent. of sulphide. Now, as in no single instance in the entire series of the experiments did any accidental circumstances occur, which even distantly approached the special conditions favourable to the oxidation of the sulphide which were introduced into these particular experiments, the authors consider themselves justified in arriving at the conclusion, that the total absence of sulphide in the residues furnished by the fine-grain powder

in experiments 40, 42, and 47, was not due to accident in the mani-
pulations, and that, in those residues in the general series of analyses
which were found to contain large quantities of hyposulphite (as in
six out of the nineteen experiments with pebble and R.L.G. powder,
and eight out of the nine with F.G. powder) the greater proportion
at any rate, of that hyposulphite existed in those particular residues
before their removal from the explosion-vessel.

In experiments which the authors have instituted with a sample of
sporting powder and one of mining powder, the following course of
proceeding was adopted for the removal of the solid residue from the
explosion-vessels, and its preparation for analysis.   Distilled water,
which had been freed from air by long-continued boiling, was syphoned
into the explosion-vessel when the latter had cooled, so that air was
never allowed to come into contact with the solid residue.   When the
cylinder was thus quite filled with water it was closed, and set aside
for sufficient time to allow the residue to dissolve completely.   The
solution was then decanted into bottles freed from oxygen, which were
quite filled with the liquid and carefully sealed up until required for
analysis.

The residues of the two experiments in which these special precau-
tions were adopted to guard against the possible accidental formation
of hyposulphite were found to contain respectively 4 and 6 per cent. of
that substance.   In the series of experiments with pebble powder
there were three, in that with R.L.G. powder four, while in that with
F.G. powder there was one, of which the residues contained propor-
tions closely similar to those furnished by these two special experi-
ments, there being no peculiarity in those seven experiments nor any
attendant circumstances which could be assigned as a possible reason
why the proportions of hyposulphite in those cases should be so much
lower than in the other experiments with the same powders carried
out under the same conditions.   The authors, therefore, cannot but
conclude that the production of a small or of a larger proportion of
hyposulphite (whether as a primary or secondary product, *but before
the explosion-vessel is opened*) is determined by some slight modifica-
tion of the conditions attending the explosion itself.

The sporting powder (Curtis and Harvey, No. 6) used by the
authors for the purpose of comparing the results of explosion with
those of the military powders used in these researches, did not differ
very widely in composition from these; the composition of the char-
coal which it contained was intermediate between those contained in
the R.F.G. and F.G. powders.   No striking points of difference were
exhibited between the proportions of the gaseous and solid products
which it furnished and those obtained with the four Service powders
used.   With the mining powder employed the case was very different.
This powder presented very important differences in composition from

any of the other powders experimented with, as well as from those used by the recent experimenters referred to in the first memoir. The proportion of saltpetre was about 11 per cent. lower than in the military powders, while the proportions of charcoal and sulphur were higher by about one-half. The composition of the former was similar to that of the pebble powder charcoal. The carbonic oxide produced from this powder was double the highest amount furnished by any of the other powders, while the carbonic anhydride, which in the three series of experiments ranged from 45 to 53 per cent., amounted only to 32 per cent., the two gases existing in about equal proportions. Marsh-gas and hydrogen were present in unusually high proportions, and the sulphuretted hydrogen amounted to 7 per cent., being nearly double the highest proportion found in all the other experiments. The solid residue presented very interesting points of difference. The potassium carbonate was, as might have been anticipated, comparatively small in amount (though some of the experiments with F.G. powder gave similar results in this respect), but there was only 0·5 per cent. of sulphate formed, while the monosulphide amounted to 33 per cent. Federow's experiments are the only ones in which so high a percentage of sulphide is recorded ; and among the several experiments with R.L.G. powder, in which only small proportions of sulphate were formed, there was only one residue in which the free sulphur was as high in amount as that formed in the mining powder-residue. The hyposulphite amounted to nearly 6 per cent.—2 per cent. more than was furnished by the sporting powder under *precisely* similar conditions of experiment, and *double* the smallest amount formed in any of the series of experiments conducted with the very special precautions which were applied in dealing with the residue of the powder under discussion. The ammonium sesqui-carbonate was considerably higher in amount than in any other experiments, and the potassium sulphocyanide amounted to 3 per cent., or about five times the amount found in any other experiment excepting that of Link. Lastly, there was a much more considerable amount of residual charcoal in this experiment than in any other.

The very distinctive peculiarities shown by the composition of the solid and gaseous products of this powder are generally such as would have been predicted from the comparatively small proportion borne by the oxidising agent to the oxidisable constituents in the mining powder.

The experiments made with mining powder presented other features of great interest in addition to those elicited by the chemical examination of the products of explosion. In concluding their observations on these, the authors point out that fresh confirmation is afforded by this experiment of the fact that hyposulphite must be classed among the invariable and more important products of explosion of gunpowder in closed spaces.

A comparative examination of the highest, lowest, and mean proportions of solid products furnished by the four military powders with which complete series of experiments (with charges ranging in gravimetric density from 0·1 to 0·9) were made, elicits various points of interest, for which reference must be made to the complete memoir.

Before quitting this portion of the subject the authors refer to a statement appended to their memoir, in which they have given the results of the following calculations :—

(1.) The amount of gaseous products, calculated from the data furnished by the analysis of the solid products.

(2.) The amount of solid products, calculated from the data furnished by the analysis of the gaseous products.

(3.) A comparison between the weights of the elementary substances found in the products of combustion and the weights of the same elements found in the powder prior to ignition.

(4.) The weight of oxygen contained in the total quantity of hyposulphite found.

An examination of this statement will show how closely accordant the various analyses, as a whole, are.

A review of the comparison between the weight of oxygen originally in the powder and that found in the products after explosion, appears to show that there is in the latter, on the average, an appreciable excess of oxygen. Hence it may pretty fairly be concluded that a portion of the hyposulphite found is due to the oxidation of the monosulphide after removal from the explosion-vessel.

On the other hand, a reference to those analyses in which hyposulphite exists in *large* proportions shows that, were the whole of the hyposulphite assumed to be formed after the removal of the products from the cylinders, there would exist a large deficiency in oxygen, and very much larger than the existing excess. Hence it may be equally fairly concluded from this line of argument that it is impossible to attribute to accidental causes the formation of the whole of the hyposulphite, and that a large proportion of it *must* be looked on either as a primary or secondary product.

In passing to a consideration of the heat generated by the explosion of gunpowder, the authors point out that, in their first memoir, they themselves called attention to the inconvenience and to the errors likely to arise from the employment of the particular form of apparatus used, and that they were at the outset fully alive to the great advantages, in regard to saving of time and labour, as well as in respect of accuracy, which would result from the use of an apparatus of the kind since employed by them. But, as one of the chief objects of their experiments was to ascertain whether the results of the metamorphosis of gunpowder, when fired in considerable quantities and under tensions similar to those developed in the bores of guns, were at all similar to

those occurring when small quantities are fired under feeble tensions, the original explosion-apparatus was designedly adopted in the earlier stages of these experiments, so as to determine the heat generated when gunpowder is fired under high tensions, for which purpose vessels of great strength and weight, and therefore not well suited for calorimetric observations, were indispensable.

A further investigation of this branch of the subject has shown, however, that the difference between the authors' earlier determinations of heat and those of other experimenters referred to by MM. Morin and Berthelot are due, not to errors in the former, but to essential differences in the decomposition of different descriptions of powder.

In continuing their heat experiments the authors made use of two explosion-vessels, similar in general form to the larger vessel described in the first memoir, but of small capacity and weight.* The specific heats of both these vessels were carefully determined, and the amount of heat absorbed by the calorimeter for various changes of temperature was also carefully determined. Thermometers specially made for the purpose, and capable of being read to $0°·01$ F. ($·006$ C.), were used in these experiments.

To determine the heat generated, a charge of from 150 to 200 grs. ($9·72$ to $12·96$ grms.) in the smaller cylinder, of 400 grs. ($25·92$ grms.) in the larger cylinder was carefully weighed and placed in the explosion-vessel. The explosion-vessel was then immersed in the water of the calorimeter and the charge fired in the usual way, the attached thermometer being read before the explosion and afterwards, continuously, until the maximum temperature (which was reached in from two to three minutes) was attained.

To make the new calorimetric determinations as complete as possible, and with the view of exhibiting the differences in the heat evolved due to differences in the composition of the powder, determinations have been made of the heat given off by the three principal powders described in the first memoir, and of three other powders differing widely in their composition, and which have been made the subject of analyses and experiments in these researches, viz. :—Ordinary English mining, Curtis and Harvey's sporting powder, No. 6, and Spanish spherical powder.

With the small explosion-vessel the mean results obtained (Experiments 146 to 166) were as follows, the numbers given below indicating the gramme-units evolved by the combustion of 1 grm. of each description of powder employed.

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* One of these weighed 1,381 grms., having a capacity of $32·5$ grms.; the other weighed 3,430 grms., and had a capacity of $118·83$ grms.

1 grm. of pebble	powder evolved	......	712·6 units.
1 ,, ,, R.L.G.	,,	,,	......	717·0 ,,
1 ,, ,, F.G.	,,	,,	......	725·7 ,,
1 ,, ,, C. & H. No. 6	,,	,,	......	754·3 ,,
1 ,, ,, Mining	,,	,,	......	508·7 ,,
1 ,, ,, Spanish	,,	,,	......	762·4 ,,

With the large explosion-vessel the results, Experiments 171 to 179
and 181 to 192, gave—

1 grm. of pebble	powder evolved	......	715·5 units.
1 ,, ,, R.L.G.	,,	,,	......	718·6 ,,
1 ,, ,, F.G.	,,	,,	.....	728·0 ,,
1 ,, ,, C. & H. No. 6	,,	,,	......	756·1 ,,
1 ,, ,, Mining	,,	,,	......	508·9 ,,
1 ,, ,, Spanish	,,	,,	......	762·3 ,,

From the whole of these experiments, and giving to the second
series, as probably the more accurate, twice the weight of the first
series, we arrive at the conclusion that the heat generated by the
combustion of the powders *as actually used* is as follows:—

1 grm. of pebble	powder generates 714·5 gramme-units.
1 ,, ,, R.L.G	,,	,,	718·1	,,
1 ,, ,, F.G.	,,	,,	727·2	,,
1 ,, ,, C. & H. No. 6	,,	,,	755·5	,,
1 ,, ,, Mining	,,	,,	508·8	,,
1 ,, ,, Spanish	,,	,,	762·3	,,

From an examination of the whole of the results it is obvious:
firstly, that the heat generated by the combustion of gunpowder is
subject to very wide variations, dependent upon the particular nature
of the powder employed (the Spanish powder for example generates
just 50 per cent. more heat than the mining powder) ; and, secondly,
that the heat evolved by the same description of powder varies in
different experiments to a greater extent than is to be accounted for
by errors of observation. And this was indeed to be expected, since
the very considerable variations in the products of combustion under
the same circumstances, as disclosed by the analyses, would hardly be
supposed to exist without some corresponding variation in the heat
evolved.

The authors' views on this head are confirmed by calorimetric deter-
minations in their researches on gun-cotton. In these determinations,
which have been carried on with precisely the same apparatus, no
appreciable difference was found in the heat evolved in the various
experiments.

The units of heat liberated, given above, are those furnished by the

powders as actually used; but as these powders had different amounts of moisture in their composition, and as, in use, these amounts of moisture are found to vary considerably, giving rise, especially when the powders are used in guns, to very different pressures and generating very different energies, it has been considered desirable to correct the above figures, the following being those that would have had place had the powders, when fired, been perfectly free from moisture.

1 grm. dry pebble	powder generates 721·4 gramme-units.
1 ,, ,, W.A.R.L.G.	,, ,, 725·7 ,,
1 ,, ,, W.A.F.G.	,, ,, 738·3 ,,
1 ,, ,, C. & H. No. 6	,, ,, 764·4 ,,
1 ,, ,, Mining	,, ,, 516·8 ,,
1 ,, ., Spanish pellet	,, ,, 767·3 ,,

In their first memoir the authors gave reasons for considering fallacious a temperature of explosion deduced (as has been done by some authors) by dividing the number of gramme-units of heat by the mean specific heat of the exploded powder at 0° C., but for purposes of comparison they give below the temperature of each powder calculated upon the above hypothesis.

Temperature of explosion of	W.A. pebble	powder	3899° C.
,, ,,	W.A.R.L.G.	,,	3880° ,,
,, ,,	W.A.F.G.	,,	3897° ,,
., ,,	C. & H. No. 6	,,	4083° ,,
,, ,,	Mining	,,	2896° ,,
,, ,,	Spanish pellet	,,	4087° ,,

The volume of the permanent gases generated by the explosion of each of the six powders is as follows (calculated for 700° C. and 760 millims. pressure, and corrected for the amounts of moisture they contained) :—

1 gramme W.A. pebble	powder generates 278·3 cub. centims.
1 ,, W.A.R.L.G.	,, ,, 274·2 .,
1 ,, W.A.F.G.	,, ,, 263·1 .,
1 ,, C. & H. No. 6	., ,, 241·0 ,,
1 ,, Mining	,, ,, 360·3 ,,
1 ,, Spanish pellet	,, ,, 234·2 ,,

It is of high importance to observe that the volume of the permanent gases generated is in every case in inverse ratio to the units of heat evolved, as is shown by the following arrangement of the results already given :—

Nature of powder.	Units of heat per gramme exploded.	Cub. centims. of gas per gramme exploded.
Spanish pellet powder	767·3	234·2
Curtis and Harvey's No. 6.	764·4	241·0
W.A.F.G.	738·3	263·1
W.A.R.L.G.	725·7	274·2
W.A. Pebble	721·4	278·3
Mining	516·8	360·3

The results given in this table are very striking. Taking the two natures of powder which commence and close the list, the heat generated by the Spanish powder is about 50 per cent. higher than that generated by the mining powder, while the quantity of permanent gases evolved by the latter is about 50 per cent. greater than that given off by the former.

Thus it appears that the great inferiority of heat developed by the mining powder, as compared with the Spanish powder, is compensated, or at least approximately so, by the great superiority in volume of permanent gases produced. A similar relation is observed in respect to the other powders, and it would indeed appear that the pressures at any given density and the capacity for performing work of the various powders are not very materially different.

This fact has been entirely verified for the whole of the Waltham Abbey powders, and in a less degree for the three other powders also.

The peculiarities shown by the mining powder are so interesting that it appeared important to determine its tension when fired under a high gravimetric density. 11,560 grs. (749 grms.) of this powder have, therefore, been fired under a gravimetric density of unity. The pressure developed by two very accordant observations was, when corrected, 44 tons on the square inch (6,706 atmospheres). The pressure obtained under similar circumstances from Waltham Abbey powder was 43 tons on the square inch (6,554 atmospheres).

It will afterwards be seen that the capacity for performing work of the various descriptions of powder was also found to be not very different, a similarity of result the more remarkable when it is remembered that with, at all events, three of the powders there were striking differences both in their composition and in the decomposition they experience, and when in consequence material variations both in pressures at different densities and in potential energy might have been expected.

With respect to the great difference in heat evolved by the Spanish and mining powders, it appears difficult to resist the conclusion that the small number of units of heat evolved by the latter is in great measure due to the quantity of heat absorbed in placing the very much

larger proportion of the products of combustion in the form of permanent gases. This suggestion would also appear fully to explain the fact alluded to in the authors' first paper, and to which they had been led purely by experiment, namely, " that the variations observed in the decomposition of gunpowder do not, even when very considerable, materially affect either its tension or capacity for performing work."

A comparison between different gunpowders, or a comparison between gunpowder and other explosive agents cannot, therefore, as has been proposed, be determined by a simple measurement of the corresponding units of heat they evolve.

Did such a law hold, the Spanish powder should have more than 50 per cent. advantage over the mining powder, but, as a matter of fact, although not very widely different, the mining powder had the advantage both in respect to the tension observed in a close vessel and to the energy developed in the bore of a gun.

As regards the *actual* temperature of explosion, the results of the further experiments detailed in this paper leave little doubt that the temperature named in the authors' first memoir, viz., 2,200° C., is not far removed from the truth for the principal powders with which they then experimented.

The slight differences or accidents which appear to give rise to not inconsiderable variations in the products of decomposition of gunpowder are obviously nearly sure to give rise to corresponding variations in the temperature of explosion, and therefore this temperature, even in one and the same powder, cannot be supposed to be always identical.

The authors then discuss the constants in the equation expressing the relation between the tension of the products of explosion and the volume these products occupy, as stated by them in their first memoir, and give values of those constants, corrected from the analyses and experiments made since the publication of that memoir, concluding their remarks upon this part of their subject with a table which gives in terms of the mean density of the powder products the tensions which would exist in the bores of guns were perfectly dry powder of normal composition suffered to expand, with or without production of work. The tensions are expressed in kilogrammes per square centimetre, tons per square inch, and atmospheres.

The authors call attention to the great utility of a table (XI) showing the theoretic work which a charge of gunpowder is capable of effecting in expanding to any value, v. The table given by them exhibits the theoretic work for all necessary volumes of v, from $v=1$ to $v=50$, and several illustrations of the use of the table are annexed.

They continue : if it be desired to know the maximum work of a given charge fired in a gun with such capacity of bore that the charge

suffered five expansions during the motion of the projectile in the gun, the gravimetric density of the charge being unity, the table shows that for every pound or kilogramme in the charge an energy of 91·4 foot-tons, or 62,400 kilogrammetres will, as a maximum, be generated. ˙

If the factor of effect for the powder be known, the above values, multiplied by that factor, will give the energy per pound or kilogramme that may be expected to be realised in the projectile.

But it rarely happens, especially with the very large charges used in the most recent guns, that gravimetric densities so high as unity are employed; in such cases from the total realisable energy must be deducted the energy which the powder would have generated had it expanded from a density of unity to that actually occupied by the charge.

Thus, in the instance above given, if we suppose the charge, instead of a gravimetric density of unity, to have a gravimetric density of ·8, which corresponds to a volume of expansion of 1·25, we see from Table XI that from the 91·4 foot-tons, or 62,400 kilogrammetres, above given, there must be subtracted 19·23 foot-tons, or 13,127·3 kilogrammetres, leaving 72·17 foot-tons, or 49,272·8 kilogrammetres, as the maximum energy realisable under the given conditions per pound, or per kilogramme, of the charge.

As before, these values must be multiplied by the factor of effect to obtain the energy realisable in the projectile.

The authors then discuss the causes which in the bore of a gun affect the energy realised by gunpowder, and point out that this energy varies very much with the powders employed, being in this respect dependent upon circumstances, such as the density of the powder, its size of grain, the amount of moisture, chemical composition, nature of charcoal used, &c., &c., but that the energy may also vary considerably even with the same powder, if the charges be not fired under precisely the same circumstances. For example, especially with slow burning powders, the weight of the shot fired exerts a very material influence upon the factor of effect, and the reason is obvious : the slower the shot moves at first, the earlier in its passage up the bore is the charge entirely consumed, and the higher is the energy realised. The same effect, unless modified by other circumstances, is produced when the charge is increased with the same weight of projectile. In this case the projectile has to traverse a greater length of bore before the same relief due to expansion is attained. The higher pressures which con-sequently rule react upon the rate of combustion of the powder, and again a somewhat higher energy is obtained.

Both these increased effects, of course, correspond to an increased initial tension of the powder-gases, but, especially with the smaller guns, a very great difference in the realised energy may arise from other causes.

Such causes, affecting the energy realised, are then discussed, and in particular the authors draw attention to the effect of retaining the shot in its seat for a greater or less time, thus giving rise in the former case to a more perfect and earlier combustion of the charge. They cite experiments to show that from this cause alone differences of energy, in guns having a calibre of 12 centims. of 13 to 14 per cent. have been obtained.

They add that in cases where the projectile has been removed for a considerable distance from the charge, that is, when there is a considerable air-space between the charge and the projectile, it has been found that the energy developed in the projectile is materially higher than that due to the expansion of the powder-gases through the space traversed by the projectile, and the cause of this appears clear; when the charge is ignited at one end of the bore, and the ignited products have to travel a considerable distance before striking the projectile, these ignited products possess considerable energy, and a portion of this energy will be communicated to the projectile by direct impact.

The authors then compare the energies realised in a gun by the various classes of powder which form the subject of their memoir, and remark that none of the powders, in realised effect, vary more from that generated by the normal Service Waltham Abbey powders, than do occasional samples of these last; a sufficiently curious result, as already remarked, when the differences in the composition and the great differences in the decomposition of the various powders are taken into account.

It is then pointed out that from the principles laid down it is possible, if the maximum chamber-pressure be known, to fix, very approximately, the position of the shot in the bore when the combustion of the charge may practically be considered to be effected.

Values of the "factor of effect" are then discussed, and the authors conclude the memoir by observing that although the agreement between the results of the long and laborious series of experiments and calculations, which they now bring to a close, have far exceeded the expectations they had formed when they commenced their task, it would yet be idle to suppose that many of their deductions, referring as they do to temperatures and tensions far above the range of ordinary research, will not require some subsequent correction.

But, although certain minor points may, as the authors have said, require considerable correction, they have little doubt that the main theories upon which they insist, confirmed as they are by experiments made, or facts obtained, under very great variety of circumstances, may be accepted as, at any rate, close approximations to the truth. It is satisfactory to find that the laws which rule the tensions and temperatures of gases under ordinary circumstances do not lose their

physical significance, but are still approximately applicable, at the high temperatures and pressures they have been considering.

At all events, whether they are right or wrong in taking this view, it appears to them certain that the rules and tables they have laid down, as based on their analyses, experiments, and calculations, may for all practical purposes be accepted as correct, and may, bearing in mind the restrictions to which they have referred in this memoir, be applied to nearly every question of Internal Ballistics.

(Received June 4, 1879.)

Since the authors completed their memoir, a charge of 10lb. of P powder has been fired in 50 per cent. space. The solid products were collected in the form of an exceedingly hard mass, weighing about 3¾lb., the fracture of which exhibited the want of homogeneity frequently alluded to by the authors. On the surface there was a deposit of varying thickness, and of a pale yellow colour, consisting chiefly of small crystals. The chemical examination of a portion of this deposit, rapidly collected, showed it to contain a considerable proportion of potassium hyposulphite. This product was exhibited to the Royal Society when the paper was read.

V. "Note on the Spectrum of Sodium."   By J. NORMAN
LOCKYER, F.R.S.   Received May 28, 1879.

I have lately been engaged in studying the spectrum of Na under new experimental conditions.

In anticipation of a detailed communication, I take leave to state that the vapour given off from the metal after slow distillation in a vacuum for some time shows the red and green lines without any trace whatever of the yellow one.

Hydrogen is given off in large quantities, and at times the C line and the red " structure" are seen alone.

After this treatment the metal, even when red hot, volatilises with great difficulty.

The Society adjourned over the Whitsuntide Recess to Thursday, June 12, the day appointed for the election of Fellows.